NBIT Final Report for AOARD Grant FA2386-10-1-4066

"**Large area graphene synthesis and its applications**"

December 10, 2013

Name of Principal Investigators:

Young Hee Lee
- e-mail address : miy16@pitt.edu
- Institution : Sungkyunkwan University
- Mailing Address : Department of Physics, Suwon 440-746, Korea
- Phone : 82-31-299-6507
- Fax : 82-31-290-5954

Moon Kim
- e-mail address : moonkim@utdallas.edu
- Institution : The University of Texas at Dallas
- Mailing Address : 800 W. Campbell Rd. RL 10, Richardson, TX 75080
- Phone : 972-883-5739
- Fax : 972-83-5725

Minhee Yun
- e-mail address : miy16@pitt.edu
- Institution : University of Pittsburgh
- Mailing Address : 218 E Benedum Hall, University of Pittsburgh
- Phone : 412-648-8989
- Fax : 412-624-8003

Period of Performance: 06/17/2010 – 12/16/2013 (include all 3 years)

Abstract: Graphene, a two-dimensional (2D) hexagonal carbon lattice is an attractive material because of because of its exceptional electrical properties, especially a high mobility combined with its mechanical and thermal stability. However, graphene applications are still limited to cases in which high defect densities and small scale random quality fluctuations can be tolerated. For the realization of graphene-based devices, we have successfully synthesized large area graphene by thermal chemical vapor deposition, characterized its morphology and physical properties by aberration corrected electron microscopy, and demonstrated various graphene-based functional nanoelectronic devices.

Introduction: The objectives of the three year project were i) to synthesize large area graphene (by Prof. Lee, Sungkyunkwan University), ii) characterize their fundamental physical and electronic properties (by Prof. Kim, The University of Texas at Dallas), iii) and utilize them for various applications such as explosive sensor, biofuel cell, Peltier device, organic solar cell, and energy storage (by Prof. Yun, University of Pittsburgh).

Results: For integration into scalable devices, Thermal Chemical Vapor Deposition (TCVD) system is the best method to growth of single and few layer graphene. We have adopted CVD growth both in ambient and in vacuum with the capability of growing large areas of single layer graphene transferrable to any desirable substrate. We have synthesized graphene on poly-nickel substrate and also Cu foil. While poly Ni substrate provides several layer graphenes, Cu foil provides a unique monolayer graphene due to the low solid solubility of

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
16 DEC 2013	**Final**	**17-06-2010 to 16-12-2013**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Large Area Graphene Systhesis and its applications (NBITPhase II)	**FA23861014066**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
Moon J Kim	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
University of Texas at Dallas,EC 33, Box 830688,Richardson 75083-0688,United States,TX,75083-0688	**N/A**
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
AOARD, UNIT 45002, APO, AP, 96338-5002	**AOARD**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)
	AOARD-104066

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Graphene, a two-dimensional (2D) hexagonal carbon lattice is an attractive material because of because of its exceptional electrical properties, especially a high mobility combined with its mechanical and thermal stability. However, graphene applications are still limited to cases in which high defect densities and small scale random quality fluctuations can be tolerated. For the realization of graphene-based devices, we have successfully synthesized large area graphene by thermal chemical vapor deposition, characterized its morphology and physical properties by aberration corrected electron microscopy, and demonstrated various graphene-based functional nanoelectronic devices.

15. SUBJECT TERMS

nano materials, nano science and technology, nano technology, Nanobiotechnology

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**Same as Report (SAR)**	**7**	

carbons in Cu. Growth temperature, gas mixing ratio of C_2H_2/H_2, and growth time were optimized to minimize the defects on graphene in addition to post annealing. High crystallinity of graphene layers with sizes up to 85 x 75 cm^2 was obtained from Cu foil. The sheet resistance can be as low as a few hundreds ohm/sq at 97 % transmittance. The sheet resistance can be further decreased by doping in particular by layer-by-layer doping technique. The best data has a sheet resistance of 54 ohm/sq at 90 % transmittance, which is the similar level to the carbon nanotube film. This meets the technical target for touch panel applications.

Before the utilization of the graphen-based devices, high resolution TEM analysis of graphene layers prepared from various sources such as natural graphite (NG), highly ordered pyrolytic graphite (HOPG) blocks, ultra thin films on Ni and Cu substrates was performed in terms of their specific characteristics. We have evaluated the morphology of CVD grown graphene in the TEM using selected area diffraction (SAD) patterns. Diffraction patterns were acquired in an array covering the entire transferred graphene sample, revealing the rotation angle of the graphene grain orientation. This rotation information was plotted and overlaid with a bright field image of the same sample in Fig. 1, illustrating what shapes the grains had and the relationship with the grains around it. With the aid of customized computer programs, we are able to acquire diffraction patterns across a whole sample and extract the lattice orientations for mapping and grain size measurements. We extended the selected area diffraction (SAD) pattern orientation mapping to include bi-layer misorientation mapping, as shown in Fig. 1(c).

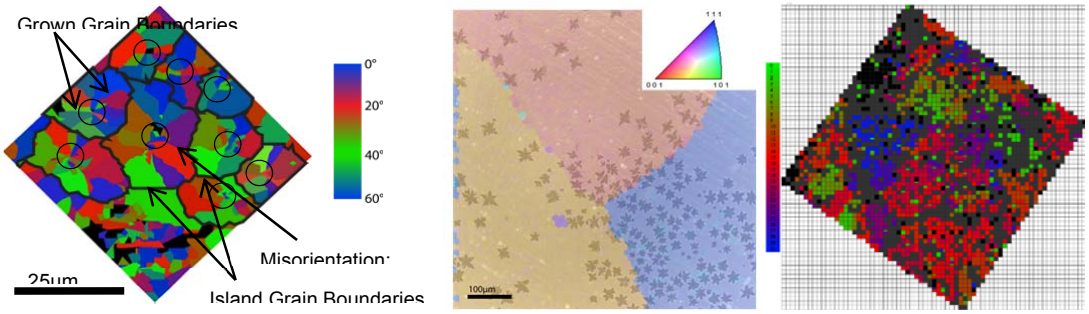

Figure 1. (Left) TEM Orientation map of a single layer graphene, showing two kinds of grain boundaries and their relative orientations. (Middle) EBSD image showing the morphological dependence of graphene grains on the Cu substrate orientation. (Right) Orientation map of double layer graphenes, showing rotational relations between two single layer graphenes.

Transferred CVD graphene was annealed in the TEM chamber up to 1200ºC to explore the effects that high temperatures have on its structure. At 1200ºC, the contamination has disappeared leaving a clear set of graphene layers. At this temperature, the edge of the flake begins to reconstruct into almost atomically straight structures as a result of the concurrent electron beam sputtering and high temperature reconstruction (Fig. 2). Our results indicate that the edge of the multi-layer graphene flake can be modified by two mechanisms that are occurring at the same time: the sputtering away of the lattice by the electron beam and the reconstruction of two monolayer edges into a bi-layer edge through high temperatures. This modifying process allows us to straighten out a multilayer flake edge on an atomic scale. We have also performed *in-situ* studies on the shrinkage and expansion of graphene nanopores under electron beam irradiation at temperatures of 400-1200ºC using a thermal specimen holder in a transmission electron microscope. The shrinkage of nanopores of various sizes is observed (Fig. 2). At all temperatures studied in the present work, nanopores

with relatively small diameters could be fully closed. We have demonstrated an approach for tailoring the size of the graphene nanopore through a combination of electron beam irradiation and controlled heat.

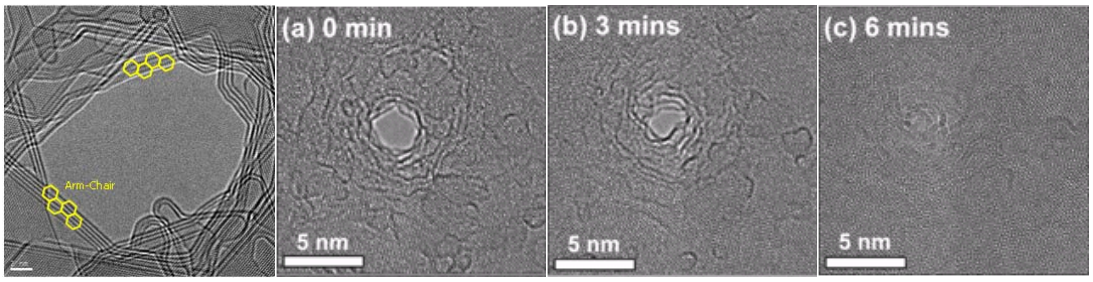

Figure 2. (Left) Reconstructed graphene edges exhibiting stable arm-chair structures. In-situ heating at 1200°C. (a-c) Controlled shrinkage of a nanopore in a graphene sheet. In-situ heating at 400°C.

The efficient removal of poly(methyl methacrylate) (PMMA) residues from the transferred graphene surface is essential for the realization of nanoelectronic devices. We have used Raman spectroscopy, x-ray photoemission spectroscopy (XPS), and transmission electron microscopy (TEM) reveal an improved removal of residual carbons by annealing in oxidative atmospheres (CO_2, O2, and NO_2), which is in sharp contrast to vacuum or reducing environments (10%H_2/90%Ar). Nevertheless, the strong oxidizing agents NO_2 and O_2 potentially react with the underlying graphene. In contrast, CO_2 is found to selectively etch PMMA residues at 500 °C without damaging graphene. Representative HRTEM images of the transferred suspended graphene before and after 500 °C annealing in CO_2 are shown in Fig. 3(a) and (b), respectively. The strategy and mechanism described here open the way for a significantly improved oxidative cleaning of transferred graphene sheets, which may require optimization tailored to specific applications.

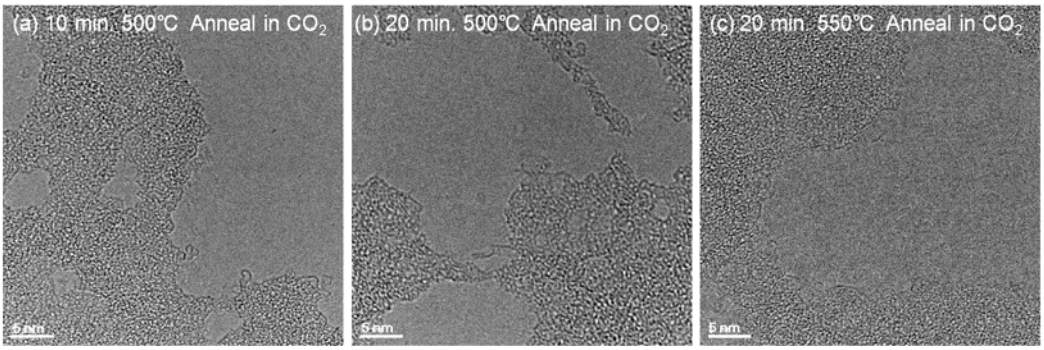

Figure 3. Representative HRTEM images of the transferred suspended graphene after 10 minutes 500 °C annealing (a), 20 minutes 500 °C annealing (b), and 20 minutes 550 °C annealing (c) in CO_2, respectively.

To subsequently utilize the unique properties of graphene, we have examined the feasibility and electrical characteristics of graphene-based devices. To reduce lateral dimensions of graphene, we examined the use of carbon nanotubes (CNTs) as a mask for narrow graphene nanoribbons (GNRs). Patterning is done via high temperature UV-irradiation (254/185 nm wavelength) of graphene masked with CNTs in an oxygen environment. Room temperature and cryogenic G_{sd}-V_g measurements of resulting nanoribbons show p-type character and field

effect $G_{On}/G_{Off} > 10^4$. The results suggest a simple route towards patterning narrow GNR with improved field effect switching.

Introducing lateral confinement via patterning of graphene nanoribbons (GNRs) with widths < 10-20 nm is one method for opening a transport gap in graphene.[1] To overcome inherent lithography limitations for low dimensional patterning, we utilized CNTs as an etch-mask for graphene. With strict control over the etch rate such that only the CNT and uncovered graphene are etched, the ultra-narrow region of graphene underneath the CNT can remain a pristine GNR. We utilized a high temperature UV-catalyzed reaction in oxygen environment to slowly etch the CNTs. Firstly, etching of sp^2 hybridized carbon via a slower oxygen functionalization and CO/CO_2 desorption requires saturating graphene with epoxy groups in a saturated environment of oxygen radicals. Carbon etching at T ~ 100° C with activation barrier ~0.45 eV is possible.[2] To achieve these saturation conditions and a very slow etch rate of graphene and CNTs, we utilized long (1 hour) UV exposures of graphene and CNT in an oxygen-only environment.

Procedurally, the etching process was done by loading samples into a closed chamber and 100 sccm of 99.999% O_2 flow maintained for 30 minutes to purge humidity and residual gases. While maintaining the O_2 flow, UV irradiation was done with a 20 mW/cm^2 low-pressure Hg lamp with 254 nm (90%) and 185 nm (10%) emission. The UV process simultaneously saturated the graphene with epoxide functional groups due to UV-induced ozone in the chamber, while also heating the chamber to at least 75° C via the same mercury lamp.

For CNTs and CNT-FETs, It was found that after 1 hour UV irradiation, all samples became insulating regardless of original metallicity (Fig. 4). To clarify whether the insulating behavior resulted from break-junctions, complete etching, or CNT flattening, AFM topography scans were performed on a CNT-FET exposed to UV for 1 hour. Zooming in on a single tube, line scans indicate the SWCNTs are truncated. From initial height of 1.5-2 nm, resulting CNTs are etched with final height between 0.4 nm and 0.9 nm. Applying the same UV procedure to graphene-only FETs, it was shown that samples become insulating after 1 hour irradiation. Physical surface interaction of the UV on graphene was elucidated by examining topography near a rip in the graphene surface prior to and after 2 hours of UV exposure. This is also shown in Fig. 4, respectively, with the rip denoted by a black-dotted line and scan locations marked by white-dotted lines. Initial line scans of the pristine monolayer graphene indicate a height near tear site of 1.3-1.4 nm. After two hours of exposure, similar scans show that the graphene surrounding the tear is etched into small islands with height ~ 1.4-1.5 nm per line scans. AFM scans also revealed that sparse regions (estimated ~1% total area) of un-etched monolayer graphene remain, with typical diameter of 1μm or less and height of ~1.4 nm, as seen in Fig. 4(e).

The ability to (i) slowly etch CNT into an insulating single/bi layer of carbon atoms while also (ii) slowly etching graphene using the same UV procedure, suggests a route to fabricate graphene nanoribbons using CNT-masking. To demonstrate this possibility, we show the time evolution of UV-irradiation on electrical properties of CNT-masked graphene FETs in Fig. 5. After 1 hour of UV irradiation, no conductance minimum was observed and overall graphene conductance decreased by a factor of $\sim 10^2$ for all Vg. Further UV exposure produced a clear off-state in the electrical characteristics, with the device acting as a unipolar p-type FET with on/off > 10^3. Hypothesized schematic for this type of behavior is shown in Fig. 5.

Cryogenic electrical properties of ultrathin GNR were also measured. G_{sd} - Vg measurements in Fig. 6 show devices having a clear electrical transport gap and a p-type G_{On}/G_{Off} ratio 10^4, respectively, at room temperature. At 80K, the second device device showed an order of magnitude decrease in conductance as depicted in Fig. 6. Note only do our devices exhibit extremely high On/Off ratio for graphene, low temperature IV shows clear existence of conductance plateaus typically manifested from coulomb charging effects and/or quantum confinement. The existence of such an effect is evidence of the extremely thin nature of the GNR.

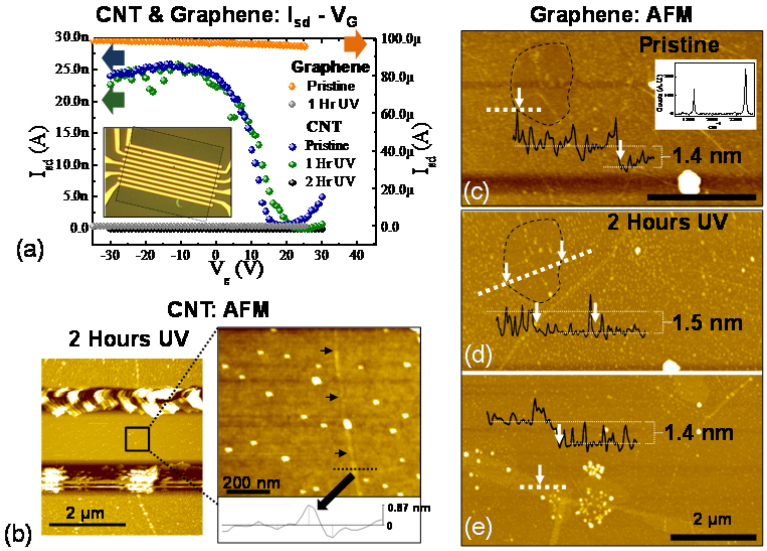

Figure 4. (a) G_{sd}-V_g by exposure time for graphene-FETs and CNT-FETs. Inset shows device optical image (b) AFM topography and line scan of a CNT device after 2 hour of UV exposure. (c) AFM of graphene before and (d) after 2 hours of UV. (e) AFM scan showing sparse un-etched regions. Black scale bar is 2 µm.

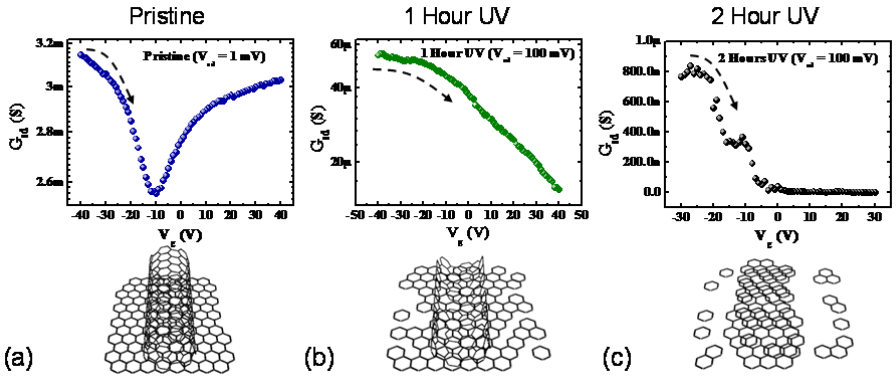

Figure 5. Electrical data for CNT/graphene hybrid structure according to UV exposure time. G_{sd}-V_g data in the (a) pristine state, (b) after 1 hour of UV, and (c) after two hours UV irradiation.

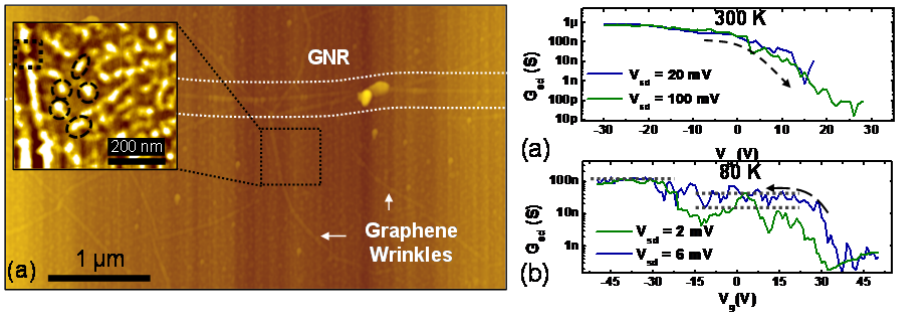

Figure 6. CNT/graphene hybrid after 2 hours of UV. (a) AFM showing wrinkles are etched into dense islands. (b) FET characteristics of GNR transistors at room temperature with G_{On}/G_{Off} and (c) 80K G_{sd}-V_g of a second device showing conductance plateaus.

The method we investigated and corresponding GNR results demonstrate a unique method to fabricate GNR using CNT as an etch mask. The GNR have excellent G_{On}/G_{Off} greater than 10^4. The UV irradiation procedure requires no solution dispersion, circumvents lithography limitations, and channel dimension depends on the density and diameter of CNTs utilized as the sacrificial masking. With careful time control, device scalability could be achieved and ribbon density controlled by varying the CVD growth conditions of the CNT or use of densely dispersed CNTs.

1. Y. W. Son, M. L. Cohen and S. G. Louie, Phys.Rev.Lett. **97**, 216803 (2006).
2. T. Sun, S. Fabris and S. Baroni, The Journal of Physical Chemistry C **115** (11), 4730-4737 (2011).

List of Publications and Significant Collaborations that resulted from your AOARD supported project:

papers published in peer-reviewed journals,

C. Gong, H.C. Floresca, D. Hinojos, S. McDonnell, X. Qin, Y. Hao, S. Jandhyala, G. Mordi, J. Kim, L. Colombo, R. Ruoff, M.J. Kim, K.J. Cho, R.M. Wallace, Y. Chabal, "Rapid Selective Etching of PMMA Residues from Transferred Graphene by Carbon Dioxide," *J. Phys. Chem*. C113, 23000-23008 (2013)

N. Lu, J.G. Wang, S. Xie, Y. Xia and M.J. Kim, "Enhanced thermal stability of Pd-Rh core–frame nanocubes: in-situ heating transmission electron microscopy," *Chem. Comm*. 49, 11806-11808 (2013).

N. Lu, J. Wang, H.C. Floresca and M.J. Kim, "In-situ studies on the shrinkage and expansion of graphene nanopores under electron beam irradiation at temperatures in the range of 400-1200°C," *Carbon* 50, 2961-2965 (2012). - Featured on the cover of journal CARBON

H.C. Floresca, D. Hinojos, N. Lu, J. Chan, L. Colombo, R.M. Wallace, J. Wang, J. Kim and M.J. Kim, "Large area mapping of graphene grain structure and orientation," *ECS Transactions* 45, 79-82 (2012)

David J. Perello, Seong Chu Lim, Seung Jin Chae, Innam Lee, Moon. J. Kim, Young Hee Lee & Minhee Yun, "Thermionic Field Emission Transport in Carbon Nanotube Transistors", *ACS NANO*, 5 (3), 1756 (2011)

H.C. Floresca, S. Mick, N. Lu, J. Wang and M.J. Kim, "Edge modification of graphene using concurrent high temperature heating and electron beam irradiation," *Microsc. Microanal*. 17 (Suppl 2), 1502-1503 (2011)

David J. Perello, Seong Chu Lim, Seung Jin Chae, Innam Lee, Moon. J. Kim, Young Hee Lee & Minhee Yun, “Current anisotropy of carbon nanotube diodes: Voltage and work function dependence”, *Appl. Phys. Lett.*, 96, 263107 (2010)

David J. Perello, Seong Chu Lim, Seung Jin Chae, Innam Lee, Moon. J. Kim, Young Hee Lee & Minhee Yun, “Anomalous Schottky Barriers and Contact Band-to-Band Tunneling in Carbon Nanotube Transistors”, *ACS Nano*, 4(6), 3103-3108 (2010)